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# Geochemistry of rare-earth elements in thermal waters of Uzon–Geyzernaya hydrothermal system (*Kamchatka*)

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**Abstract**

Precisional analyses of the abundances of La, Ce, and major elements in thermal waters and rocks of the Uzon–Geyzernaya volcanotectonic depression, supplemented by published data on a number of modern high-temperature hydrothermal systems of Kamchatka and two other areas of the world, allowed defining genetically important patterns of rare-earth elements (REE) distribution. The La and Ce abundances positively correlate with silica contents both in fresh igneous rocks of the study areas and in the products formed by hydrothermal processes. All studied hydrothermal clays are enriched in La and Ce. The general enrichment trend is similar to the pattern of positive correlation between the La and Ce abundances. Geothermal waters display a strong relationship between REE enrichment and pH. Enhanced REE enrichment trend is observed in thermal waters with abundant $SO_4^{2-}$ and K. The REE versus Cl and B diagrams show two individual fields reflecting the level of acidity–alkalinity of thermal waters. These data demonstrate that La and Ce concentrations in the products of modern hydrothermal systems (in fluids and secondary mineral phases) are governed by wallrock composition, anionic water composition, and pH/Eh-dependent adsorption processes.


*Keywords:* Uzon Caldera; rare-earth elements; thermal waters; thermal fields; hydrothermal clays

## Introduction

The behavior of rare-earth elements (REE) in modern hydrothermal systems has become of renewed interest because of an increased demand for REE in the realm of material technology and increased analytical capacity for detecting REE concentrations in rocks and natural waters (Inguaggiato et al., 2015; Marshall and Marshall, 2015). ICP-MS and related modern techniques allow performing precisional analyses of REE abundances in rocks and waters over a great number of natural sites.

High REE concentrations in the hydrothermal systems of Kamchatka, Russia were recently reported by the reconnaissance of Karpov (2004), Karpov et al. (2013, 2015) where they suggest that REE were transported to discharge areas along with subneutral Cl- and Na-rich fluids coming from the deepest portions of the volcanic system. Areas of sulfur-bearing compounds oxidation show REE enrichment of both thermal waters and mineral sediments (Karpov et al., 2015).

Our work has been focused on the analyses of REE distribution patterns in various types of thermal waters, including ultra-acidic types, with a particular emphasis on correlating La and Ce abundances to the altered wall rocks and mineral sediments.

The similarity between $La^{3+}$ and $Ce^{3+}$ atomic radii (~1.02 Å) and the redox sensitivity of Ce (i.e., $Ce^{3+}$ versus $Ce^{4+}$) allow for examination of pH and Eh partitioning effects that might be active in terrestrial hot spring systems. Such basic relationships seen in the rocks and the temperature, pH, and geochemistry of spring fluids may offer insights to the general behavior of all REE and how they might be redistributed in hydrothermal systems.

## Study area and methods

The paper is based upon the data gathered by the authors within the frameworks of a 2012–2015 joint Russian–American Project, supplemented by the results of long-term surveys

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conducted by many scientists of the Institute of Volcanology and Seismology FEB RAS and other institutions in the thermal fields of Uzon–Geyzernaya hydrothermal system (Fig. 1). We also include geochemical data on hot springs of Akademii Nauk Caldera, mud pots and lake basins of Mutnovsky and Maly Semyachik volcano craters, thermal occurrences of the Geyser Valley and Kikhpinych volcano (Bortnikova et al., 2009; Eroshchev-Shak et al., 1998; Grib et al., 2003, 2009; Nikolaeva et al., 2015). For comparison, data on a submarine smoker located in the Rainbow area (Atlantic Ocean) were used, as well as those on thermal springs of Nevada del Ruiz (Colombia) (Inguaggiato et al., 2015).

Representative samples were collected from Uzon Caldera (Fig. 2) that hosts vast thermal fields exhibiting intense hydrothermal activity. The numerous and varied occurrences of thermal waters make this site unique within the Kamchatka Peninsula (Dobretsov et al., 2015; Karpov, 1974, 1988; Karpov and Pavlov, 1976; Pilipenko, 1974; and others). The sites in Uzon Caldera include hot and boiling springs, mud pots and volcanoes, sulfur melts at the bottom of the Bannoe Lake, steaming and heated grounds punctured with gas vents and active geysers, and minor oil occurrences (Karpov and Fazlullin, 1995; Kyle et al., 2007). Springs show temperature ranges of 20 to 97 °C and total salinity ranges of 0.5 to 2.9 g/L. Most springs operate in a pulsating outflow regime, with some occasionally changing into geysers and others going quiescent (Karpov et al., 2012). The frequency of the oscillations is thought to be related, in part, to the activity of the long-lived magmatic chamber located at the depth of 5–7 km (Moroz et al., 2014). It can also be attributed to the tectonic fissures whose width varies affected by frequent small local earthquakes (Dobretsov et al., 2015). Shorter time scale oscillations may also occur from diurnal solar cycles, synoptic weather fronts, and lunar Earth-tides cycles, all of which can be suggested by temperature data logged for nearly one year in two springs (Arkashin and Skovorodka) in Uzon Caldera. Thermo-buttons were placed in tethered perforated plastic test tubes weighted with gravel fill and preprogramed to record temperature at ~10 minute intervals. Standard MatLab Fourier Transform routines were employed to determine significant periodicities. It has been noted that weather observations from Elizovo airport show monthly averages of 7 to 10 rain days per month consistently throughout the year, thus suggesting synoptic periodicity of similar time scales.

Sediments were collected on site and stored in sealed vials. Volcanic rocks representative of the region were also collected as hand samples. Waters were collected on site using standardized methods (Wilde et al., 1998) whereby samples were immediately passed through 0.22 μm syringe filters and collected in sealed vials. Field measures of temperature and pH were made with a digital probe thermometer and calibrated ion selective meter, respectively.

Select chemical analysis of water samples was carried out following standard anion chromatographic and cationic atomic absorption procedures in the Analytical Centre of the Institute of Volcanology and Seismology (IVS) FEB RAS. Microelement abundances in solutions were determined by Element-2 induction coupled plasma mass spectrometer (ICP-MS) at Moscow State University. Sediment samples were analyzed using an S4-PIONEER X-ray fluorescence spectrometer.

## Results

Felsic volcanics in Uzon–Geyzernaya volcanic-tectonic depression hosting the hydrothermal system of the same name (Fig. 1) include dacites, rhyodacites, andesites and their tuffs. Less commonly basalts occur.

Most igneous rocks commonly show low abundances of La and Ce, with maximum values reported in rhyodacites (Ta-

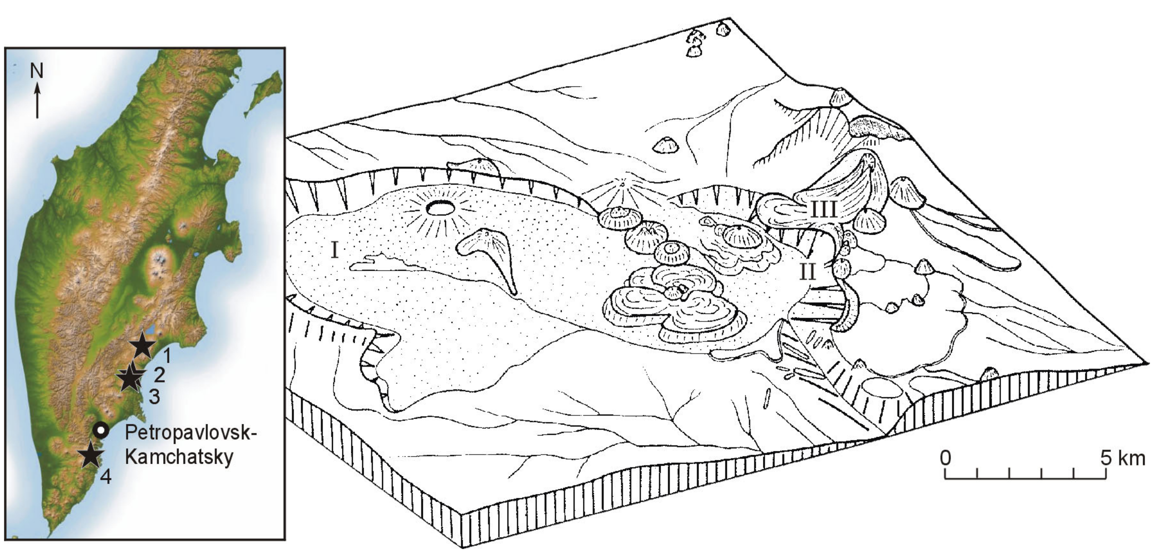


Fig. 1. Map of Uzon–Geyzernaya volcanic-tectonic depression by (Leonov and Grib, 2004). Research sites (insert right): I, Uzon Caldera; II, Valley of Geysers; III, Kikhpinych volcano. Inset: map of the Kamchatka Peninsula. Numbered stars mark sampled hydrothermal systems (insert left): 1, Uzon–Geyzernaya; 2, Maly Semyachik volcano; 3, Akademii Nauk caldera; 4, Mutnovsky volcano area.

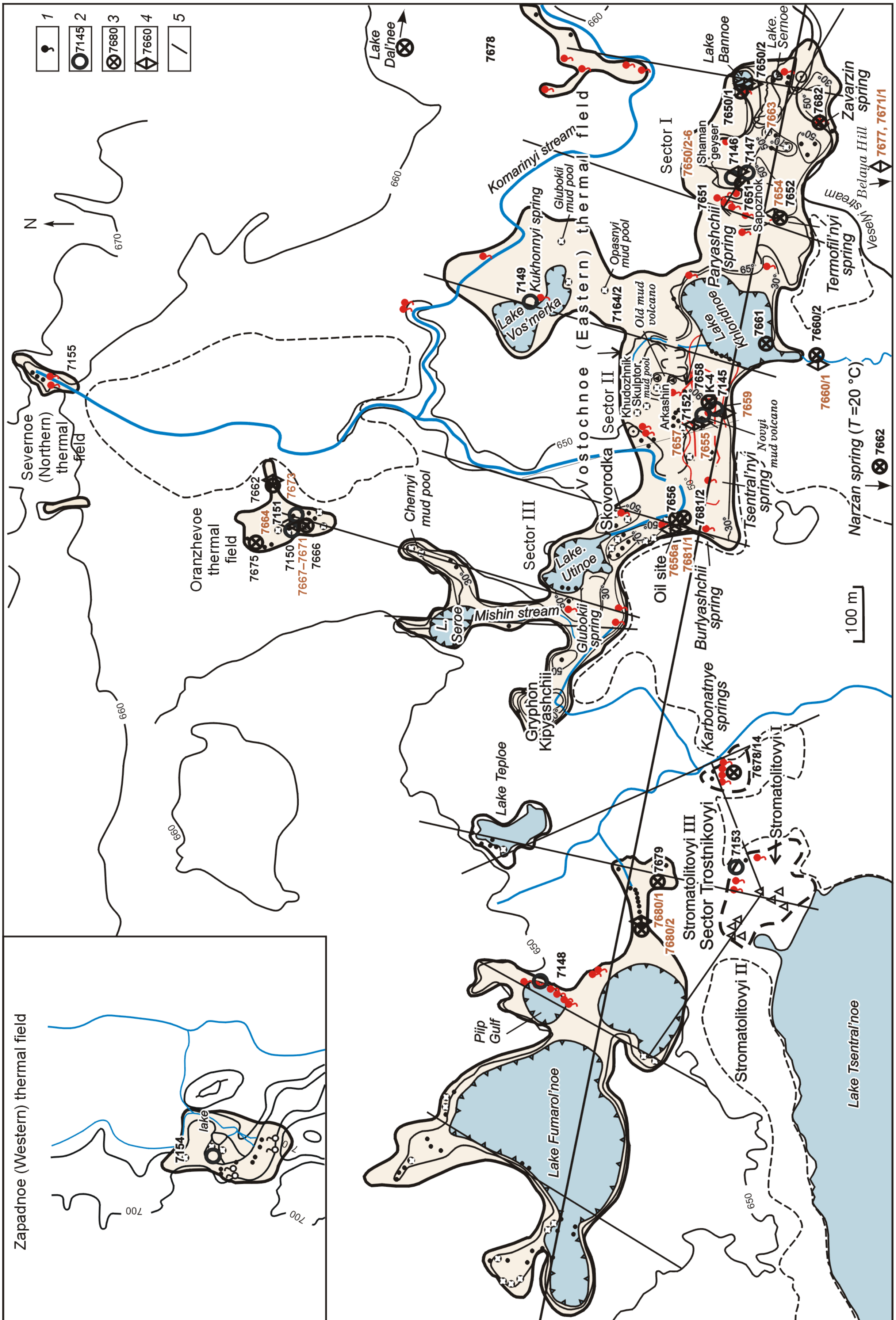


Fig. 2. Detailed map of thermal occurrences and sampling sites in Uzon Caldera (Karpov, 1988). *1*, thermal springs, 2, sites and reference numbers of water probes in 2013; 2, the same in 2014; *4*, sites and reference numbers of sediment samples in 2014; *5*, faults.

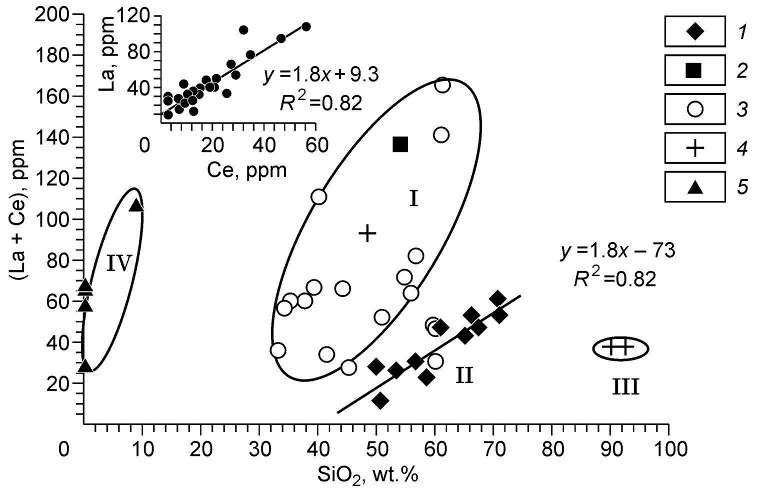


Fig. 3. (La + Ce) versus $SiO_2$ concentrations in rocks from Uzon–Geysernaya hydrothermal system. *1*, igneous rocks (basalts, andesites, dacites, ryodacites); *2*, psephitic tuff; *3*, hydrothermal clays, silts; *4*, geyserites; *5*, calcites. Inset: Positive correlation of La/Ce in igneous and altered rocks of Kamchatka.

ble 1). Chemical analysis of all types of igneous and altered rocks from the region reveals a high positive correlation between La and Ce ($R^2 = 0.82$) with a slope of about 2 (Fig. 3, inset), which is the evidence of the nearby redox environment. A plot of wt.% $SiO_2$ versus ppm La + Ce values for volcanic rock samples (Fig. 3, Trend II) shows a positive correlation ($R^2 = 0.82$) with a slope of 1.8. This suggests a near doubling of (Ce + La) content with every 10% increase in $SiO_2$ for rocks in the study area.

The highest contents of REEs for Uzon Caldera have been reported in argillizites and gravelites with sulfide mineralization found in the upper layers of the profile cut in the Central Sector of the Eastern thermal field, as well as in clays and ejecta from numerous mud volcanoes (Table 1).

Anomalously high REE abundances corresponding to gravelites and argillizites form Field I in the center of the plot (Fig. 3). Particularly high contents of La and Ce have been reported in hydrothermal clays from the Oranzhevoe (Orange) field (up to 56.5 ppm La and 108.5 ppm Ce). Anomalously high concentrations of Ce in these smectite-rich clays (Fackrell, 2015) quite agree with the reducing environments of their formation we reported earlier. Field I also includes a La- and Ce-rich point that corresponds to the fresh geyserite of Shaman geyser whose composition shows the presence of fine iron sulfides, which is the evidence of high reducing potential of its waters and presence of $H_2S$ in their composition (Karpov et al., 2012). Much lower concentrations of REE reported in ancient geyserites of Akademii Nauk springs fall into Field III. Hydrothermal calcites of the Valley of Geysers and thermal waters beneath the Kikhpinych volcano show high concentrations of REE (Field IV), which is quite natural given the genetic affinity of Ca, La, and Ce.

Analyses of REE abundances in thermal waters of the study areas provide valuable information regarding their genesis. Maximum values of La and Ce contents have been reported in brackish and acidic waters of Bannoe Lake (Uzon Caldera) and in the saline ultraacid thermal waters of complex mineral composition, which include Troitskoe Lake at Maly Semyachik volcano and waters from mud pots in the Mutnovsky volcano crater (Table 2). Hydrothermal solutions display a general trend of increasing REE concentration with decreasing pH (Karpov et al., 2013; Michard, 1989), however

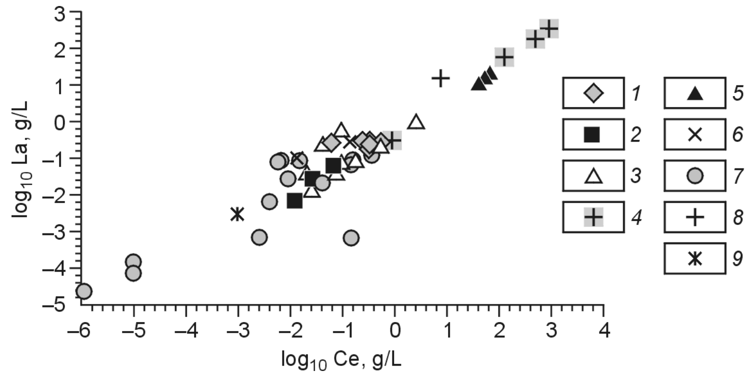


Fig. 4. La versus Ce concentrations in thermal waters of Kamchatka and other regions. *1*, Uzon Caldera; *2*, Valley of Geysers; *3*, Akademii Nauk Caldera; *4*, Mutnovsky volcano area; *5*, Maly Semyachik volcano (Troitskoe Lake); *6*, local atmospheric precipitations; *7*, Nevada del Ruiz (Colombia); *8*, Rainbow thermal field (Atlantic Ocean); *9*, seawater.

Table 1. Abundances of $SiO_2$ and REE (La and Ce) in representative rocks of Kamchatka

| No. | Sample number | Study area | Sampling site | Rock type | $SiO_2$ | La | Ce |
|---|---|---|---|---|---|---|---|
| | | | | | % | ppm | |
| 1 | 44 | Uzon Caldera | Western thermal field* | Basalt | 49.94 | 7.80 | 20.00 |
| 2 | 5 | | Belaya Hill (extrusion)* | Dacite | 65.17 | 11.00 | 32.00 |
| 3 | K-1/03 | | Dal'nee Lake** | Andesite | 56.74 | 8.52 | 21.59 |
| 4 | 11-91 | Kikhpinych volcano | Southern Sector** | Basalt | 50.56 | 2.98 | 8.14 |
| 5 | 446-75 | Valley of Geysers (VG) | "Geyzernaya" extrusion** | Andesite | 61.10 | 13.65 | 34.17 |
| 6 | 515-78 | | | Dacite | 66.28 | 15.32 | 37.86 |
| 7 | 312-74 | | | Ryodacite | 70.80 | 17.90 | 43.28 |
| 8 | 1024 | Karymsky Volcanic Center (KVC) | Karymskaya Caldera (western rim)*** | Andesite | 58.50 | 7.16 | 16.00 |
| 9 | K7-04 | | Karymskaya Caldera*** | Dacite | 67.36 | 14.47 | 32.58 |
| 10 | K10-96 | | Akademii Nauk Caldera*** | Pumice bomb | 70.90 | 15.34 | 37.30 |
| 11 | 7663 | Uzon Caldera | Bannoe Lake area**** | Psephitic tuff | 54.00 | 32.32 | 104.26 |
| 12 | 7162/1 | | New mud volcano (Eastern thermal field)**** | Clays | 37.70 | 26.00 | 34.00 |
| 13 | 7161 | | Old mud volcano (Eastern thermal field)**** | | 40.30 | 35.00 | 76.00 |
| 14 | 7549 | | Vos'merka Lake**** | | 54.70 | 22.00 | 50.00 |
| 15 | 7164/1 | | Mud pot near Vos'merka Lake**** | | 44.30 | 18.00 | 48.00 |
| 16 | 7164/2 | | Opasnyi mud pot**** | | 35.20 | 21.00 | 39.00 |
| 17 | 7165 | | Khudozhnik mud pot | | 34.40 | 19.00 | 38.00 |
| 18 | 7548 | | Fumarol'noe Lake**** | | 60.20 | 11.00 | 36.00 |
| 19 | 7552 | | Mud pot near the Observation site**** | | 60.00 | 3.00 | 28.00 |
| 20 | 7667 | | Oranzhevoe thermal field | | 56.70 | 29.29 | 53.20 |
| 21 | 7668 | | | | 61.10 | 46.46 | 94.50 |
| 22 | 7669 | | | | 61.40 | 56.56 | 108.50 |
| 23 | 83 | VG | Verkhnegeyzernoe thermal field**** | | 45.24 | 3.00 | 25.00 |
| 24 | 357 | Kikhpinych volcano | Southern thermal field**** | | 39.40 | 21.00 | 46.00 |
| 25 | 7296 | KVC | Staryi geyser area (Akademii Nauk srings)**** | | 59.90 | 15.00 | 33.00 |
| 26 | 7300 | | Water–mud pool "Anna"**** | | 55.80 | 20.00 | 44.00 |
| 27 | 7650 | Uzon Caldera | Bannoe Lake**** | Silts | 41.60 | 7.07 | 27.30 |
| 28 | 7660 | | Khloridnoe Lake outflow**** | | 33.30 | 12.12 | 23.80 |
| 29 | 7680 | | Fumarol'noe Lake outflow**** | | 50.70 | 9.09 | 43.40 |
| 30 | 7651/5 | | Shaman geyser**** | Geyserites | 48.50 | 27.27 | 65.80 |
| 31 | 5563 | KVC | Stenka geyser (Akademii Nauk springs)**** | | 90.12 | 11.00 | 27.00 |
| 32 | 5560 | | Stary geyser (Akademii Nauk springs)**** | | 92.48 | 11.00 | 27.00 |
| 33 | 372c | VG | Verkhnegeyzernoe thermal field**** | Calcites | 0.12 | 9.00 | 20.00 |
| 34 | 373a | | Verkhnegeyzernoe thermal field**** | | 0.12 | 7.00 | 61.00 |
| 35 | 378a | | Averiy spring**** | | 0.15 | 4.50 | 62.00 |
| 36 | 7294 | Kikhpinych volcano | Karbonatnyi spring (Akademii Nauk springs)**** | | – | 0.00 | 58.00 |
| 37 | 756a1 | | Southern thermal field**** | | 8.92 | 4.50 | 103.00 |

Note. *, Data by (Eroshchev-Shak et al., 1998), **, (Grib et al., 2003); ***, (Grib et al., 2009); ****, our data; hereafter, dash—no data available.

the specific behavior of La and Ce is also complicated by the concentrations of anions ($SO_4^{2-}$, $Cl^-$) and adsorption onto mineral surfaces (Wood and Shannon, 2003). Ce and La concentrations for water data in Table 2 vary on orders of magnitude, whereby a linear regression of log-Ce versus log-La (Fig. 4) shows a good positive fit of $y = 0.82x - 0.1$ ($r^2 = 0.93$).

In circum-neutral and alkaline thermal waters (La + Ce) values are quite low ranging 0.45–0.88 ppm in springs and 0.16–0.72 ppm in geyser waters. (La + Ce) values in alkaline geyser waters are somewhat lower than those in subneutral hot-spring waters, which, apparently, reflects not only the characteristics of the acid-base properties of solutions, but also the degree of their gas saturation, and, accordingly, the

Table 2. Abundances of major and trace elements in thermal waters of Kamchatka

| No. | Sample number | Sampling site | $T$, ºC | pH | Major elements | | | | | | Trace elements | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | $K^+$ | $Ca^{2+}$ | $Cl^-$ | $SO_4^{2-}$ | $HCO_3^-$ | B | La | Ce |
| | | | | | mg/L | | | | | | μg/L | |
| Uzon Caldera | | | | | | | | | | | | |
| 1 | KV-55 | Bannoe Lake (Rn-discharge site)* | 42.0 | 6.89 | 6.3 | 24.0 | 9.9 | 96.1 | 48.8 | 0.087 | 0.241 | 0.333 |
| 2 | KV-56 | Khloridnoe Lake** | 30.0 | 5.50 | 32.7 | 39.1 | 587.0 | 336.8 | 1.0 | 14.865 | 0.178 | 0.323 |
| 3 | KV-59 | Antimonitovyi spring* | 96.0 | 7.50 | 197.0 | 48.0 | 2450.0 | 54.2 | 58.0 | 89.087 | 0.272 | 0.552 |
| 4 | KV-58 | Real'garovyi spring** | 78.0 | 6.98 | 33.0 | 40.1 | 990.7 | 229.0 | 75.6 | 46.935 | 0.295 | 0.238 |
| 5 | KV-67 | Tsentral'nyi spring* | 97.5 | 7.5 | 78.2 | 44.1 | 1932.6 | 105.7 | 0.6 | 57.957 | 0.078 | 0.137 |
| 6 | KV-57 | Narzan spring** | 20.8 | 5.92 | 9.9 | 63.1 | 20.6 | 134.5 | 469.8 | 0.227 | 0.295 | 0.337 |
| Valley of Geysers and Geysernaya River upper course | | | | | | | | | | | | |
| 7 | 4588 | Velikan geyser** | 91.0 | 9.30 | 63.3 | 20.8 | 794.3 | 158.5 | 60.4 | 18.695 | 0.028 | 0.027 |
| 8 | 4592 | Zhemchuzhnyi geyser* | 95.0 | 8.49 | 59.1 | 22.0 | 794.3 | 182.5 | 61.6 | 19.028 | 0.063 | 0.068 |
| 9 | 4589 | Averiy spring** | 97.0 | 8.00 | 3.3 | 10.5 | 65.9 | 15.5 | 18.2 | 6.051 | 0.007 | 0.012 |
| Akademii Nauk Caldera | | | | | | | | | | | | |
| 10 | 5/05-K | Mud pot No. 5** | 95.0 | 4.29 | 7.8 | 37.3 | 0.7 | 230.5 | 0.0 | 0.682 | 1.035 | 2.534 |
| 11 | 7470 | Novyi geyser** | 97.2 | 9.49 | 16.4 | 3.2 | 429.1 | 105.7 | 46.4 | 8.849 | 0.250 | 0.042 |
| 12 | KMCh-21/05 | Staryi geyser** | 87.0 | 9.30 | 16.7 | 3.6 | 365.2 | 92.2 | 58.6 | 8.621 | 0.014 | 0.026 |
| 13 | KMCh-15/05 | Pechka geyser** | 95.9 | 9.50 | 10.1 | 5.6 | 184.4 | 67.2 | 42.7 | 3.637 | 0.043 | 0.021 |
| 14 | 4715 | Pulsating Eastern spring*** | 88.0 | 9.10 | 16.10 | 3.20 | 340.40 | 96.10 | 75.70 | 7.345 | 0.078 | 0.094 |
| 15 | KMCh-21/05 | Karbonatnyi spring** | 95.0 | 7.45 | 10.5 | 26.1 | 212.7 | 45.6 | 252.6 | 4.092 | 0.043 | 0.076 |
| 16 | 4708 | Plyazhnye springs** | 47.0 | 5.82 | 7.8 | 29.7 | 74.5 | 74.5 | 201.7 | 0.856 | 0.089 | 0.179 |
| 17 | KMCh-27/05 | Piipovskie springs (No. 1)* | 71.2 | 7.76 | 19.9 | 46.1 | 305.0 | 306.4 | 72.0 | 3.182 | 0.128 | 0.290 |
| 18 | 4707 | Bottom vent (Karymskoe Lake) | 40.0 | 7.55 | 11.4 | 37.70 | 74.80 | 153.7 | 50.00 | 1.189 | 0.227 | 0.518 |
| Mutnovsky geothermal area | | | | | | | | | | | | |
| 19 | SDP-4 | Bottom field (Mutnovsky volcano, mud pots)*** | 83.0 | 0.18 | 120.0 | 53.0 | 13000.0 | 2700.0 | 0.0 | 9.100 | 55.000 | 130.000 |
| 20 | SDP-5 | | 84.0 | –0.03 | 740.0 | 170.0 | 32000.0 | 8.5 | 0.0 | 32.000 | 340.000 | 920.000 |
| 21 | SDP-9* | | 75.0 | –0.11 | 380.0 | 120.0 | 15000.0 | 2200.0 | 0.0 | 17.000 | 170.000 | 490.000 |
| 22 | Gk-2/D | Dachnye springs (mud pot)* | 91.1 | 3.06 | 6.2 | 20.0 | 0.7 | 230.5 | 0.0 | 0.000 | 0.307 | 0.891 |
| Maly Semyachik volcano | | | | | | | | | | | | |
| 23 | KV-68 | Troitskoe Lake* | 35.7 | 1.38 | 26.9 | 360.7 | 1633.0 | 2332.6 | 0.0 | 4.109 | 16.186 | 52.698 |
| 24 | KV-69 | | 35.0 | 1.42 | 25.0 | 344.7 | 1576.2 | 2693.5 | 0.0 | 5.841 | 20.690 | 67.694 |
| 25 | KV-71 | | 37.0 | 1.20 | 21.2 | 376.8 | 1617.0 | 2070.1 | 0.0 | 5.229 | 11.915 | 42.952 |
| Local atmospheric precipitation | | | | | | | | | | | | |
| 26 | KV-50 | Rainfall (Uzon Caldera)** | 10.0 | 7.10 | 0.1 | 3.2 | 1.0 | 2.4 | 11.0 | 0.017 | 0.274 | 0.140 |
| 27 | 4604 | Rainfall (Akademii Nauk Caldera)** | 12.0 | 6.90 | 0.4 | 2.0 | 0.7 | 2.9 | 2.0 | 0.122 | 0.101 | 0.014 |
| The Nevado del Ruiz volcano-hydrothermal system (Colombia)**** | | | | | | | | | | | | |
| 28 | G-1 | Agua Hedionda | 13.9 | 5.9 | 2.7 | 30.5 | 1.8 | 97.0 | 140.3 | – | 0.0001 | 0.00001 |
| 29 | G-2 | Rio Molinos | 15.9 | 8.8 | 7.8 | 57.3 | 50.7 | 172.9 | 73.2 | – | 0.00002 | 0.000001 |
| 30 | G-3 | Nereidas | 50.4 | 6.1 | 17.6 | 130.3 | 22.0 | 297.8 | 573.4 | – | 0.0002 | 0.00001 |
| 31 | G-4 | Botero Londono | 79.5 | 7.7 | 82.1 | 48.1 | 1006.9 | 65.3 | 85.4 | – | 0.0007 | 0.0027 |
| 32 | G-5 | Termal La Gruta | 33.5 | 1.6 | 55.1 | 177.1 | 514.1 | 3544.8 | 0.0 | – | 0.0892 | 0.1544 |
| 33 | G-6 | Hotel 1 | 59.8 | 1.4 | 70.0 | 241.7 | 737.4 | 5005.0 | 0.0 | – | 0.0646 | 0.1449 |
| 34 | G-7 | Hotel 2 | 62.6 | 1.4 | 75.5 | 256.1 | 776.4 | 5398.9 | 0.0 | – | 0.0007 | 0.1471 |
| 35 | G-8 | Agua clainete | 59.3 | 1.0 | 226.0 | 246.5 | 1265.7 | 10586.4 | 0.0 | – | 0.1270 | 0.3608 |

(*continued on next page*)

Table 2 (*continued*)

| No. | Sample number | Sampling site | *T*, °C | pH | Major elements | | | | | | Trace elements | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | $K^+$ | $Ca^{2+}$ | $Cl^-$ | $SO_4^{2-}$ | $HCO_3^-$ | B | La | Ce |
| | | | | | mg/L | | | | | | μg/L | |
| 36 | G-9 | Quebrada La Gruta | 15.3 | 2.1 | 33.6 | 60.9 | 174.8 | 1210.4 | 0.0 | – | 0.0204 | 0.0425 |
| 37 | G-10 | Agua Blanco | 29.1 | 3.3 | 10.2 | 416.0 | 49.3 | 1546.6 | 0.0 | – | 0.0874 | 0.0151 |
| 38 | G-11 | Rio Lagunillias | 6.8 | 3.6 | 1.2 | 16.4 | 3.2 | 134.5 | 0.0 | – | 0.0069 | 0.0040 |
| 39 | G-12 | Rio Guali | 7.2 | 3.5 | 6.3 | 107.4 | 28.0 | 554.3 | 0.0 | – | 0.0283 | 0.0092 |
| 40 | G-13 | Rio Azufrado | 16.0 | 3.4 | 15.2 | 165.3 | 54.6 | 1546.6 | 0.0 | – | 0.0785 | 0.0060 |
| 41 | G-14 | FT Gauli | 59.2 | 2.8 | 10.9 | 347.5 | 46.1 | 1508.2 | 0.0 | – | 0.0832 | 0.0067 |
| 42 | 6 | Rainbow hydrothermal field (Atlantic ocean)***** | 365.0 | 2.8 | 20.0 | 67.0 | 750.0 | – | – | – | 15.557 | 7.686 |
| 43 | 1/D | Seawater***** | 2.0 | 7.8 | 387.0 | 408.0 | 19354.0 | 2225.0 | 142.3 | 4.529 | 0.003 | 0.001 |

Note. *, Data by (Karpov et al., 2014); **, our data; ***, (Bortnikova et al., 2009); ****, (Inguaggiato, 2015); *****, (Dubinin, 2006). Dash, no data available.

oxidation reduction potential (Dobretsov et al., 2015). Ce concentrations predominate over La in all of the studied thermal waters and igneous rocks. The fractionation of light even REE seems typical for areas of recent active volcanism (Inguaggiato et al., 2015; Karpov et al., 2013).

The placement of La + Ce abundance into groups is well displayed by the diagram of log (La + Ce) versus pH (Fig. 5). In general, abundances for higher values are in the ultraacid area (pH ≤ 2.0) and lower values in circum-neutral and alkaline area (pH ≥ 5.5). Line I groups the studied hydrothermal systems of Kamchatka, whereas line II includes all hot springs of Colombia (Inguaggiato et al., 2015) and a submarine hot spring of the Rainbow field (Dubinin, 2006).

Definite trend of REE abundances correlation to $SO_4^{2-}$ in thermal waters is seen in Fig. 6*a*. Similar relations have been reported for (La + Ce)/K (Fig. 6*c*), which is quite explicable given the presence of K, Na, and Li in the composition of deep Cl-Na fluids. Plots for (La + Ce)/Cl and (La + Ce)/B show the following grouping of thermal waters: group I includes all acid waters, whereas subneutral and alkaline waters form group II (Fig. 6*b*, *d*).

Temperature dependence of La + Ce distribution pattern in thermal waters is not well pronounced (Fig. 7), which can be attributed to significant contribution of cool surface waters mixing into the hydrothermal waters as a function of weather conditions. This is indirectly evidenced by the temperature surveys we conducted for Arkashin and Skovorodka springs (Fig. 8). Here, temperature increase (i.e., intensified by deep thermal waters) correlates with season changes. The highest (La + Ce) values occur in waters with the highest temperatures.

## Discussion

The behavior of REE in geothermal systems is noted to be related to (1) rock composition, (2) anionic composition of waters, (3) composition of secondary minerals, and (4) adsorption processes related to the zero point of charge on solid surfaces (which is a function of solution pH) (Brookins, 1989; Inguaggiato et al., 2015; Karpov et al., 2013; Wood and Shannon, 2003). Thus we suggest that La and Ce in Uzon and similar hydrothermal systems are mainly transported by subalkaline waters bearing significant portions of a deep Cl–Na component. In this regard, the most representative is Uzon Caldera whose deep-derived supply from a shallow magma chamber is evidenced by both geophysical data (Moroz et al., 2014) and by some petrochemical surveys. Thus, Goodner (2014) examined glasses from the maar hosting the Dal'nee Lake (Uzon Caldera) and noted that their compositions were typical of the subduction zone magmas. However, his petrographic and chemical analysis from the study cannot reject a hypothesis that the maar was formed due to magma–groundwater interaction.

Of practical importance are data on total yield of REE from thermal fields. The largest streams draining the Uzon thermal fields flow down from Fumarol'noe and Khloridnoe Lakes (Fig. 2). Dissolved load calculations, using discharge and

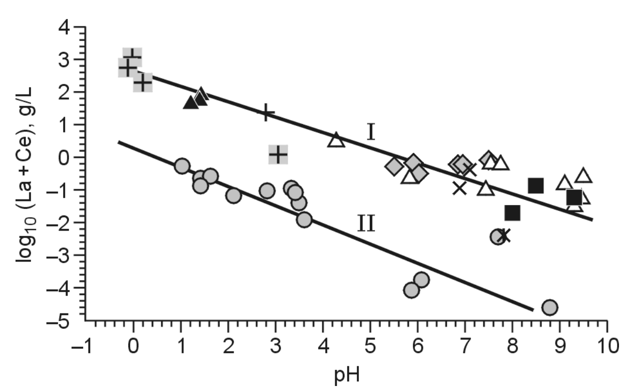


Fig. 5. Log (La + Ce) concentrations versus pH in thermal waters of Kamchatka and other regions. Lines I and II are described in the text. For legend see Fig. 4.

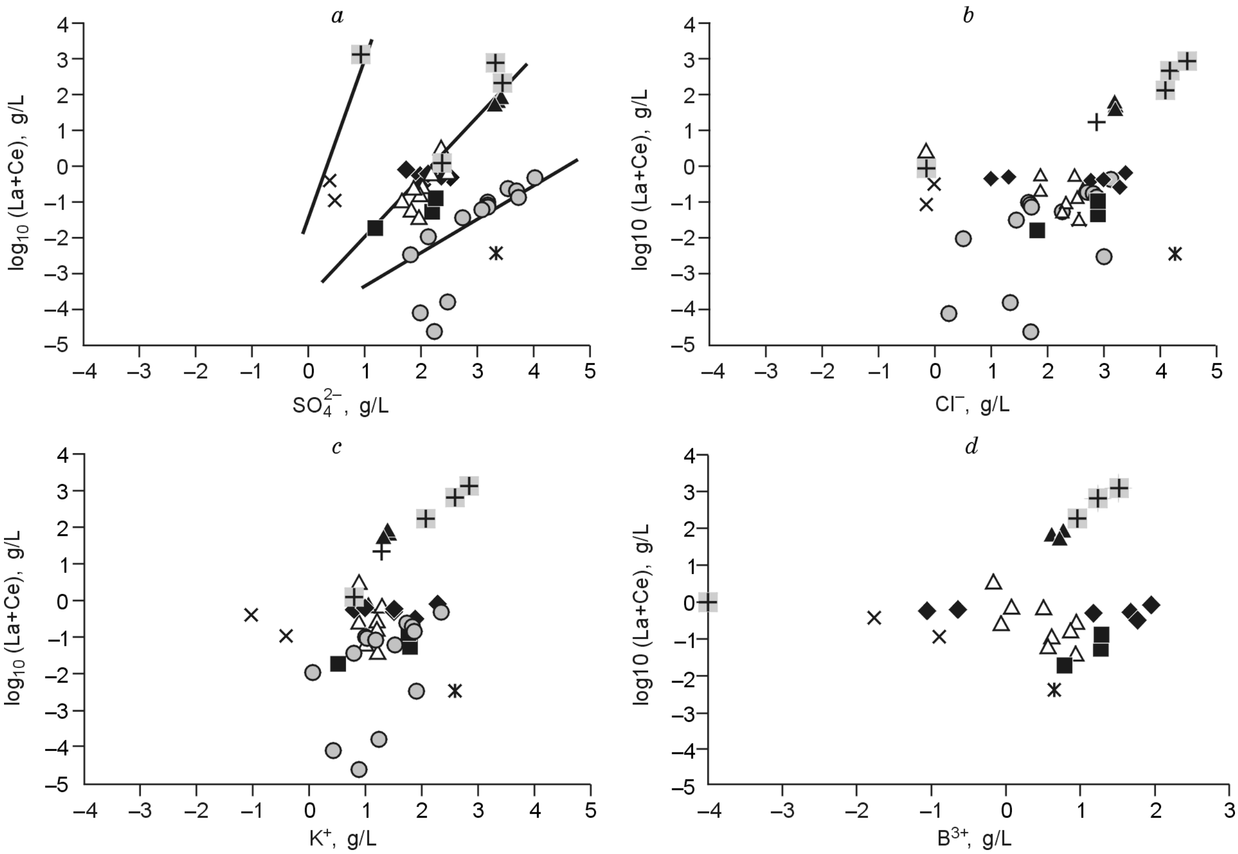


Fig. 6. Log (La + Ce) versus $SO_4^{2-}$ (*a*), $Cl^-$ (*b*), $K^+$ (*c*), $B^{3+}$ (*d*) in thermal waters. For legend see Fig. 4.

concentrations for these areas, yield about 12 kg/year of (La + Ce) (Table 3). These streams flow to a subsedimentary basin within the caldera and then most of the streams coalesce into Tsentral'noe (Central) Lake, which unites the surface zones of all Uzon's hydrothermal discharges.

The stream draining the Oranzhevoe field whose clays and thermal waters have shown the highest concentrations of REE also flows into Tsentral'noe Lake. Dissolved load yield of (La + Ce) from the Oranzhevoe field in the head of the watershed is much lower, which is accounted for by the low discharge rate of the Oranzhevyi Stream (0.5 L/s). La/Ce ratio of the Oranzhevoe field is much lower than the two other lakes. Test-pits made in clays enriched in sulfur compounds revealed highly acidic thermal waters where Ce concentrations were much higher relative to those of La. The mechanism for this trend is the formation of secondary oxidized Fe and S phases (i.e., jarosite, kaolinite, goethite). Such minerals can form in microbial communities and are able to persist for a long time in the rocks (Lazareva et al., 2012). All of them also can incorporate La and Ce either as adsorbed species

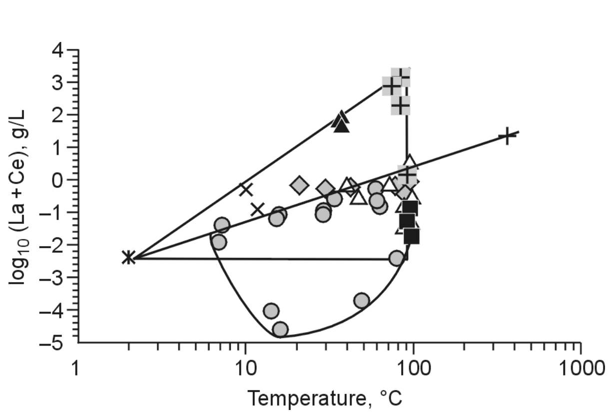


Fig. 7. Temperature relation ship with $\log_{10}(La + Ce)$ abundances in thermal waters of Kamchatka and other regions. For legend see Fig. 4.

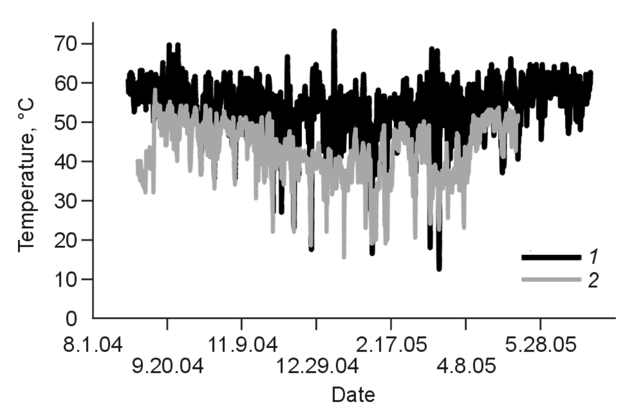


Fig. 8. Temperature data logger for two thermal hot springs in the Uzon Caldera eastern thermal sector (Arkashin (*1*) and Skovorodka (*2*)) in Uzon Caldera from August 1, 2004 till May 28, 2005.

Table 3. Yield of La and Ce from thermal lakes and fields of Uzon Caldera (August 2014)

| Sample number | Sampling site | *T*, °C | pH | *Q*, L/s | Abundance | | Yield | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | µg/L | | mg/s | | kg/year | | |
| | | | | | La | Ce | La | Ce | La | Ce | La + Ce |
| 7680 | Fumarol'noe Lake outflow | 23.0 | 2.60 | 84.0 | 0.2 | 0.67 | 0.020 | 0.056 | 0.630 | 1.770 | 2.400 |
| 7660 | Khloridnoe Lake outflow | 27.0 | 3.10 | 345.0 | 0.2 | 0.67 | 2522.4 | 7253.2 | 2.520 | 7.250 | 9.770 |
| 7672 | Oranzhevoe field outflow | 24.5 | 2.30 | 0.5 | 0.5 | 1.61 | 0.0003 | 0.008 | 0.008 | 0.025 | 0.033 |

or as substitutions in the mineral structure (Alarcon et al., 2014).

The calcitic samples have low La contents relative to Ce, however their concentrations are high. In this case, bicarbonate becomes an important anion-ligand complex, so that efficient sequestering takes place at circum-neutral to alkaline conditions.

We suggest that the pulsing nature of hydrothermal systems is an important forcing function that allows the oxidation states of the Ce to be varied, hence changing its mobility relative to La. In the ultra-acidic systems, Ce is not differentiated from La, as they behave similarly. The sulfate-rich and chloride-rich waters serve to provide anion-ligands with La and Ce.

The pH dependence of (La + Ce) seen in Fig. 5 suggests that congruent dissolution of these elements is coming from deep within the igneous rocks. The Kamchatka trend in Fig. 5 parallels the trend seen in the hydrothermal system of Colombia (Inguaggiato et al., 2015).

The higher values of (La + Ce) in Kamchatka relative to Colombia can be attributed to differences in the subducting rock compositions and the extent of partial melting and fractional crystallization occurring in the magmatic arc systems.

More recently, Kalacheva et al. (2016) have noted the additional complexities of boiling-condensation mixing processes in acidic waters of the hydrothermal system of Ebeko volcano (Paramushir Island) located within the Kurile–Kamchatka island arc. Ebeko REE trends with Sr isotopic compositions suggest congruent dissolution of deep volcanic fluid due to mixing with a shallow aquifer. Water–mud pools at the Ebeko volcano (pH = 1–2) also show abundances of REEs (La + Ce) similar to those of the Mutnovsky volcano (Bortnikova et al., 2009) and Colombia (Inguaggiato et al., 2015).

## Conclusions

The fluids in the Kamchatka hydrothermal systems show a wide range of (La + Ce) compositions that correlate with an equally wide range of pH conditions.

Igneous rocks of the Kamchatka peninsula show a linear trend of increasing (La + Ce) content with increasing silica content (basalts to rhyodacites). Hydrothermally altered rocks of the studied hydrothermal systems show a general trend of (La + Ce) enrichment with silica depletion related to the hydrolysis.

A high correlation between pH and (La + Ce) abundances in thermal waters supports the notion of congruent dissolution of igneous rocks from deep within the volcanic system induced by hydrothermal solutions.

Anomalously high contents of (La + Ce) in clays can be attributed to adsorption on clay minerals and incorporation into nanocrystalline oxy/hydroxy, sulfate, and sulfide phases.

Pulsing of the hydrologic flux through the geothermal system is enhanced by cycles of deep magmatic activity, diurnal solar heating/cooling, synoptic high/low pressure events, and possibly lunar/earth tides. These pulses promote temperature and redox conditions of the environment controlling REE enrichment in thermal waters.

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